

What is claimed is:

1. A method of forming a metal thin film, comprising:

forming an oxygen-deficient metal oxide film on a semiconductor substrate by atomic layer deposition (ALD) using an organic metal compound as a first reactant, wherein the oxygen-deficient metal oxide film comprises a metal oxide having an oxygen content that is less than a stoichiometric amount; and

forming a metal oxide film on the oxygen-deficient metal oxide film by ALD using the first reactant and a second reactant, wherein the second reactant comprises an oxidizing agent.

2. The method according to claim 1, wherein the first reactant comprises an alkoxide-based metal oxide.

3. The method according to claim 1, wherein the first reactant comprises a lanthanum-containing compound.

4. The method according to claim 3, wherein the first reactant is selected from the group consisting of tris(1-n-propoxy-2-methyl-2-propoxy)lanthanum (III) ($\text{La}(\text{NPMP})_3$), tris(2-ethyl-1-n-propoxy-2-butoxy)lanthanum (III) ($\text{La}(\text{NPEB})_3$), lanthanum (III) ethoxide ($\text{La}(\text{OCH}_2\text{H}_5)_3$), tris(6-ethyl-2,2-dimethyl-3,5-decanedionato)lanthanum (III) ($\text{La}(\text{EDMDD})_3$), tris(dipivaloylmethanate)lanthanum (III) ($\text{La}(\text{DPM})_3$), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lanthanum (III) ($\text{La}(\text{TMHD})_3$), lanthanum (III) acetylacetonate ($\text{La}(\text{acac})_3$), and tris(ethylcyclopentadienyl)lanthanum (III) ($\text{La}(\text{EtCp})_3$), or combinations thereof.

5. The method according to claim 1 further comprising:

(a) feeding the first reactant onto the semiconductor substrate to form an adsorbed layer of the first reactant;

(b) removing a byproduct of (a) by means of purge; and

(c) optionally repeating (a) and (b) until the oxygen-deficient metal oxide film with a predetermined thickness is formed.

6. The method according to claim 1, wherein the oxygen-deficient metal oxide film has a thickness in a range of about 5Å to about 30Å.

7. The method according to claim 1, further comprising:

5 (a) feeding the first reactant onto the semiconductor substrate having the oxygen-deficient metal oxide film thereon, to form a chemisorbed layer of the first reactant;

(b) feeding the second reactant onto the chemisorbed layer to form the metal oxide film; and

10 (c) optionally repeating (a) and (b) until the metal oxide film with a predetermined thickness is formed.

8. The method according to claim 7, wherein the second reactant is selected from the group consisting of O₃, O₂, plasma O₂, H₂O, and N₂O, or combinations thereof.

9. The method according to claim 7, further comprising removing a byproduct after (a) and removing a byproduct after (b).

20 10. The method according to claim 9, wherein the removal of the byproduct is carried out by means of inert gas purge.

11. The method according to claim 1, wherein the method is carried out at a temperature in a range of about 200°C to about 350°C.

25 12. The method according to claim 1 further comprising annealing the oxygen-deficient metal oxide film.

30 13. The method according to claim 12, wherein the annealing is carried out after forming the oxygen-deficient metal oxide film or after forming the metal oxide film.

14. The method according to claim 12, wherein the annealing is carried out at a temperature in a range of about 300°C to about 800°C.

15. The method according to claim 12, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O₂, N₂, and O₃, or combinations thereof, or under a vacuum atmosphere.

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16. A method of forming a lanthanum oxide film, comprising:
forming a first lanthanum oxide film on a semiconductor substrate by atomic layer deposition (ALD) using an alkoxide-based organic metal compound as a first reactant, wherein the first lanthanum oxide film comprises La₂O_x wherein x<3 ; and
10 forming a second lanthanum oxide film comprising La₂O₃ on the first lanthanum oxide film by ALD using the first reactant and a second reactant, wherein the second reactant comprises an oxidizing agent.

17. The method according to claim 16, wherein the first reactant is selected from the group consisting of La(NPMP)₃, La(NPEB)₃, and La(OC₂H₅)₃, or combinations thereof.

18. The method according to claim 16 further comprising:
(a) feeding the first reactant onto the semiconductor substrate to form an adsorbed layer of the first reactant;
20 (b) removing a byproduct of (a) by means of purge; and
(c) optionally repeating (a) and (b) until the first lanthanum oxide film with a predetermined thickness is formed.

19. The method according to claim 18, wherein the first lanthanum oxide film has a thickness in a range of about 5Å to about 30Å.

20. The method according to claim 16 further comprising:
(a) feeding the first reactant onto the semiconductor substrate having the first lanthanum oxide film thereon, to form a chemisorbed layer of the first reactant;
30 (b) feeding the second reactant onto the chemisorbed layer to form the second lanthanum oxide film; and
(c) optionally repeating (a) and (b) until the second lanthanum oxide film with a predetermined thickness is formed.

21. The method according to claim 20, wherein the second reactant is selected from the group consisting of O₃, O₂, plasma O₂, H₂O, and N₂O, or combinations thereof.

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22. The method according to claim 20, further comprising removing a byproduct after (a) and removing a byproduct after (b).

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23. The method according to claim 22, wherein the removal of the byproduct is carried out by means of inert gas purge.

24. The method according to claim 16, wherein the method is carried out at a temperature in a range of about 200°C to about 350°C.

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25. The method according to claim 16 further comprising annealing the first lanthanum oxide film.

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26. The method according to claim 25, wherein the annealing is carried out after forming the first lanthanum oxide film or after forming the second lanthanum oxide film .

27. The method according to claim 25, wherein the annealing is carried out at a temperature in a range of about 300°C to about 800°C.

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28. The method according to claim 25, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O₂, N₂, and O₃, or combinations thereof, or under a vacuum atmosphere.

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29. A method of forming a high dielectric film, comprising:
forming a first dielectric film on a semiconductor substrate, wherein the first dielectric film comprises a first metal oxide; and
forming a second dielectric film on the first dielectric film, wherein the second dielectric film comprises a second metal oxide, and wherein the method of forming the second dielectric film comprises:

(a) forming an oxygen-deficient metal oxide film on the first dielectric film by atomic layer deposition (ALD) using an organic metal compound as a first reactant, wherein the oxygen-deficient metal oxide film comprises the second metal oxide and the second metal oxide has an oxygen content that is less than a stoichiometric amount; and

(b) forming a metal oxide film on the oxygen-deficient metal oxide film by ALD using the first reactant and a second reactant, wherein the second reactant comprises an oxidizing agent.

30. The method according to claim 29, wherein the first dielectric film comprises Al_2O_3 .

31. The method according to claim 29, wherein the first dielectric film is formed by chemical vapor deposition (CVD) or ALD.

32. The method according to claim 29, wherein the first dielectric film has a thickness in a range of about 30Å to about 60Å.

33. The method according to claim 29, wherein the first reactant comprises an alkoxide-based metal oxide.

34. The method according to claim 29, wherein forming the oxygen-deficient metal oxide film comprises:

(a) feeding the first reactant onto the first dielectric film to form an adsorbed layer of the first reactant;

(b) removing a byproduct on the semiconductor substrate by means of purge; and (c) optionally repeating (a) and (b).

35. The method according to claim 29, wherein the oxygen-deficient metal oxide film has a thickness in a range of about 5Å to about 30Å.

36. The method according to claim 29, wherein forming the metal oxide film comprises:

(a) feeding the first reactant onto the semiconductor substrate having the oxygen-deficient metal oxide film thereon, to form a chemisorbed layer of the first reactant;

(b) feeding the second reactant onto the chemisorbed layer to form the metal oxide film; and

(c) optionally repeating (a) and (b).

37. The method according to claim 36, wherein the second reactant is selected from the group consisting of O₃, O₂, plasma O₂, H₂O, and N₂O, or combinations thereof.

38. The method according to claim 36, further comprising removing a byproduct after forming the chemisorbed layer of the first reactant and removing a byproduct after forming the metal oxide film.

39. The method according to claim 38, wherein the removal of the byproduct is carried out by means of inert gas purge.

40. The method according to claim 29, wherein (a) and (b) are carried out at a temperature in a range of about 200°C to about 350°C.

41. The method according to claim 29 further comprising annealing the oxygen-deficient metal oxide film.

42. The method according to claim 41, wherein the annealing is carried out after forming the oxygen-deficient metal oxide film or after forming the metal oxide film on the oxygen-deficient metal oxide film.

43. The method according to claim 41, wherein the annealing is carried out at a temperature in a range of about 300°C to about 800°C.

44. The method according to claim 41, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O₂, N₂, and O₃, or combinations thereof, or under a vacuum atmosphere.

5 45. A method of forming a high dielectric film, comprising:
forming a first dielectric film on a semiconductor substrate, wherein the first dielectric film comprises a metal oxide; and

forming a second dielectric film on the first dielectric film, wherein the second dielectric film comprises a lanthanum oxide, and wherein the method of forming the
10 second dielectric film comprises:

(a) forming a first lanthanum oxide film on a semiconductor substrate by atomic layer deposition (ALD) using an alkoxide-based organic metal compound as a first reactant, wherein the first lanthanum oxide film comprises La₂O_x, wherein x<3; and

15 (b) forming a second lanthanum oxide film comprising La₂O₃ on the first lanthanum oxide film by ALD using the first reactant and a second reactant, wherein the second reactant comprises an oxidizing agent.

20 46. The method according to claim 45, wherein the first dielectric film comprises Al₂O₃.

47. The method according to claim 45, wherein the first dielectric film is formed by CVD or ALD.

25 48. The method according to claim 45, wherein the first dielectric film has a thickness in a range of about 30Å to about 60Å.

30 49. The method according to claim 45, wherein the first reactant is selected from the group consisting of La(NPMP)₃, La(NPEB)₃, La(OCH₂H₅)₃, La(EDMDD)₃, La(DPM)₃, La(TMHD)₃, La(acac)₃, and La(EtCp)₃, or combinations thereof.

50. The method according to claim 45, wherein the method of forming the first lanthanum oxide film comprises:

feeding the first reactant onto the first dielectric film to form an adsorbed layer of the first reactant;

5 removing a byproduct on the semiconductor substrate by means of purge; and

optionally repeating (a) and (b).

51. The method according to claim 45, wherein the first lanthanum oxide
10 film has a thickness in a range of about 5Å to about 30Å.

52. The method according to claim 45, wherein the method of forming the second lanthanum oxide film comprises:

(a) feeding the first reactant onto the semiconductor substrate having the first
15 lanthanum oxide film thereon, to form a chemisorbed layer of the first reactant;

(b) feeding the second reactant onto the chemisorbed layer to form the second lanthanum oxide film; and

optionally repeating (a) and (b).

20 53. The method according to claim 52, wherein the second reactant is selected from the group consisting of O₃, O₂, plasma O₂, H₂O, and N₂O, or combinations thereof.

25 54. The method according to claim 52, further comprising removing a byproduct after forming the chemisorbed layer of the first reactant and removing a byproduct after forming the second lanthanum oxide film.

55. The method according to claim 54, wherein removal of the byproduct is carried out by means of inert gas purge.

30 56. The method according to claim 45, wherein (a) and (b) are carried out at a temperature in a range of about 200°C to about 350°C.

57. The method according to claim 45 further comprising annealing the first lanthanum oxide film.

58. The method according to claim 57, wherein the annealing is carried out after forming the first lanthanum oxide film and after forming the second lanthanum oxide film.

59. The method according to claim 57, wherein the annealing is carried out at a temperature in a range of about 300°C to about 800°C.

60. The method according to claim 57, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O₂, N₂, and O₃, or combinations thereof, or under a vacuum atmosphere.

61. A metal thin film formed by the method according to claim 1.

62. The metal thin film according to claim 61, wherein the metal thin film is capable of preventing the formation of a low dielectric layer at an interface between the metal thin film and an electrode.

63. A semiconductor device comprising the metal thin film according to claim 61.

64. A lanthanum oxide film formed by the method according to claim 16.

65. A semiconductor device comprising the lanthanum oxide film according to claim 64.

66. A high dielectric film formed by the method according to claim 29.

67. A semiconductor device comprising the high dielectric film according to claim 66.

68. A high dielectric film formed by the method according to claim 45.

69. A semiconductor device comprising the high dielectric film according to claim 68.